ν_{max} (potassium bromide pellet) 1686 (conjugated carbonyl) and 893 cm.$^{-1}$ (epoxide).

Base-catalyzed Reactions of *t*-Butyl Hydroperoxide with Isophorone.—Isophorone (0.10 mole) and *t*-butyl hydroperoxide (0.25 mole) were allowed to react in benzene solution in the presence of Triton-B (0.005 mole). After 18 hours at room temperature, the reaction mixture was washed with water. The aqueous washings were saturated with salt and extracted with ether. The combined organic layers were dried over anhydrous magnesium sulfate and evaporated. The residue consisted primarily of starting ketone, along with a small amount of product. This mixture could not be separated on a spinning band column.[5]

From the aqueous washings, after acidification and extraction with ether, there was isolated 0.43 g. of an acid. This acid was distilled in a Kragen tube at 0.03 mm. (bath temperature approximately 95°), n^{21}D 1.4492. It was not further characterized.

This acid also was isolated from the reaction of isophorone in aqueous medium with alkaline hydrogen peroxide.[18]

Base-catalyzed Reaction of *t*-Butyl Hydroperoxide with 4-Cholesten-3-one.—When 4-cholesten-3-one (3.85 g., 0.01 mole) was treated with *t*-butyl hydroperoxide (2 ml., 0.018 mole) in benzene solution in the presence of Triton-B (0.0002 mole) for 4 hours at room temperature and 19 hours at 50°, the starting ketone was recovered.

When 4-cholesten-3-one (1.93 g., 0.005 mole) was treated with Triton-B (0.0005 mole) in 15 ml. of *t*-butyl hydroperoxide as solvent for 19 hours at room temperature, the starting ketone was again recovered.

16α,17α-Epoxy-4-pregnen-3,20-dione.—16-Dehydroprogesterone (1.0 g., 0.0032 mole), *t*-butyl hydroperoxide (0.6 ml., 0.0054 mole) and Triton-B (0.05 g. of a 35% methanolic solution, 0.0001 mole) were dissolved in 6 ml. of benzene and allowed to stand for 12 hours at room temperature. The reaction mixture was then washed 3 times with water. The aqueous washings were saturated with salt and extracted with ether. The combined organic layers were dried over anhydrous magnesium sulfate and, after evaporation of the solvents at reduced pressure, there was obtained 0.98 g. (93%) of a white crystalline solid, m.p. 165–183°. The infrared spectrum of the analytical sample was indistinguishable from that of the crude product. After recrystallization from methanol there was obtained 0.59 g. of crystals, m.p. 205–207°, $[\alpha]^{27}$D +156.6° (34.0 mg. in 5 ml. chloroform), αD +2.13° (*l* 2 dm.) (lit.[6] m.p. 205–207°), $[\alpha]^{27}$D +160.8° (34.5 mg. in 5 ml. chloroform), αD +1.11° (*l* 1 dm.); ν_{max} (potassium bromide pellet) 1700 (saturated carbonyl), 1665 (unsaturated carbonyl), 1613 (conjugated double bond, and 885 cm.$^{-1}$ (epoxide)).

From the mother liquor was obtained an additional 0.09 g. of pure product, m.p. 204–206° (total yield 65%). From the aqueous washings was isolated, after appropriate treatment, 0.04 g. of an unidentified acidic material.

The Base-catalyzed Reaction of *t*-Butyl Hydroperoxide with β-Nitrostyrene.—β-Nitrostyrene (7.45 g., 0.05 mole) and *t*-butyl hydroperoxide (7.5 ml., 0.068 mole) were dissolved in 75 ml. of benzene at ice-bath temperature. Triton-B (0.48 g. of a 35% methanolic solution, 0.001 mole) was added and after a few minutes a precipitate was observed. The mixture was warmed to room temperature and stirred an additional 90 minutes before the precipitate was collected on a filter. There was obtained 6.56 g. of a powdery white solid which melted at 200–210° with some charring. This material was insoluble in the usual solvents. A similar polymeric material precipitated almost immediately when Triton-B (2 mole %) was added to a benzene solution of β-nitrostyrene.[7,8] When β-nitrostyrene and *t*-butyl hydroperoxide were mixed in ether solution in the presence of 4 mole % of triethylamine, no reaction was observed after 20 hours at room temperature. However, when the reaction mixture was warmed during evaporation of the solvent, the formation of polymeric material was observed.

***t*-Butyl 2-Cyanoethyl Peroxide.**—Following the method of Harman,[4] acrylonitrile (2.0 ml., 0.03 mole) slowly was added with stirring to a solution containing 11 ml. (0.10 mole) of *t*-butyl hydroperoxide, 2.9 ml. of water and 0.9 ml. of 40% aqueous potassium hydroxide. After stirring 0.5 hour at room temperature, the two phases were separated and the upper (organic) layer washed several times with distilled water. The organic layer was then dried and distilled at reduced pressure. After removal of the forerun, which was identified as *t*-butyl hydroperoxide, there was obtained 0.93 g. (22%) of product, b.p. 57–59° (1.4 mm.), n^{20}D 1.4189 (lit.[4] n^{20}D 1.4142); ν_{max} (pure liquid) 2268 (saturated nitrile), 1383, 1366 and 1244 cm.$^{-1}$ (*t*-butyl group).

Anal. Calcd. for $C_7H_{13}O_2N$: C, 58.72; H, 9.15; mol. wt., 143.18. Found: C, 58.81; H, 9.39; mol. wt., 140.

The same product was obtained in 18% yield when the reaction was carried out in dilute aqueous solution.

Methyl 3-*t*-Butylperoxypropionate.—To a stirred solution of methyl acrylate (9.1 ml., 0.10 mole) and *t*-butyl hydroperoxide (15 ml., 0.135 mole) in 175 ml. of benzene was added 1.44 g. of a 35% methanolic solution of Triton-B (0.003 mole) in small portions over a period of one hour at ice-bath temperature. The reaction mixture was then allowed to warm to room temperature. After 8 hours, an additional 1.44 g. of 35% methanolic Triton-B solution was added. After being allowed to remain an additional 12 hours at room temperature, the reaction mixture was worked up in the usual manner. The product, after fractionation through a 60 × 0.7 cm. tantalum wire column, weighed 3.91 g. (22%), b.p. 75° (13 mm.), n^{25}D 1.4140 (lit.[4] n^{20}D 1.4142); ν_{max} (pure liquid) 1748 (saturated carbonyl), 1383, 1366 and 1244 cm.$^{-1}$ (*t*-butyl group).

Anal. Calcd. for $C_8H_{16}O_4$: C, 54.53; H, 9.15; mol. wt., 176.21. Found: C, 54.55; H, 9.11; mol. wt., 175.

When the reaction was carried out at room temperature for 12 hours in dilute aqueous solution there was obtained a 2.2% yield of product, which was identified by its infrared spectrum.

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[18] Ketone cleavage presumably occurred; see H. O. House and R. L. Wasson, *J. Org. Chem.*, **22**, 1157 (1957).

[CONTRIBUTION FROM THE TEXACO RESEARCH CENTER]

Mechanism of the Dehydrocyclization of *n*-Heptane

BY JOHN J. MITCHELL

RECEIVED MAY 16, 1958

The mechanisms already in the literature for the dehydrocyclization of *n*-heptane to toluene all predict that the dehydrocyclization of *n*-heptane-1-C^{14} would produce toluene with 50% of the C^{14} in the methyl group. One run, at conditions which gave a product containing 56 mole per cent. toluene, gave 27 ± 1% of the C^{14} in the toluene methyl group; another, at conditions yielding a product containing 74 mole per cent. toluene, gave 29 ± 1% of the C^{14} in the methyl group. Two possible mechanisms leading to this lower value of methyl C^{14} content and a test to distinguish between them are proposed.

Introduction

The mechanism of catalytic dehydrocyclization has been the subject[1] of considerable study because the process is one of obvious commercial, as well as scientific, importance. It was shown quite early after the discovery of dehydrocyclization that, in the conversion of *n*-heptane to toluene, *n*-

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[1] See the review of C. Hansch, *Chem. Revs.*, **53**, 353 (1953).

heptene is a necessary intermediate. Pitkethly and Steiner[2] argued that the *n*-heptene re-adsorbed at the double bond, was half-hydrogenated, and then was converted to a cyclic biradical which went over to adsorbed methylcyclohexane. The methylcyclohexane desorbed and lost hydrogen simultaneously to become toluene. Herington and Rideal[3] held that the *n*-heptene was chemisorbed with opening of the double bond and two-point attachment and that a six-membered ring formed to give the equivalent of adsorbed methylcyclohexene which then desorbed and lost hydrogen simultaneously. Wheatcroft,[4] on the other hand, was of the opinion that the *n*-heptene was adsorbed at a part of the molecule remote from the double bond and that ring closure was brought about by reaction between a double-bond carbon and one of the adsorbed positions in the molecule.

All three of these mechanisms agree in postulating that 1-heptene or 2-heptene or both are the necessary intermediates. If one were to start out with *n*-heptane-1-C^{14}, then, aside from a possible small isotope effect, the 1-heptene produced as an intermediate would be an equal mixture of 1-heptene-1-C^{14} and 1-heptene-7-C^{14} and the 2-heptene would be an equal mixture of 2-heptene-1-C^{14} and 2-heptene-7-C^{14}. Thus, all three mechanisms would predict that *n*-heptane-1-C^{14} would lead to toluene with half of the original C^{14} in the methyl group and half in the *o*-position in the ring.

This paper reports the results of a test of this prediction. *n*-Heptane-1-C^{14} was passed over a chromia-on-alumina catalyst. The toluene produced was separated from the other product materials by distillation and then oxidized to benzoic acid. The benzoic acid was decarboxylated, and the resulting CO_2 assayed for C^{14}. The C^{14} activity was compared to that in the starting *n*-heptane-1-C^{14} to see if indeed half of the C^{14} did enter the methyl group.

Experimental

_n_-Heptane-1-C^{14}.—The *n*-heptane-1-C^{14} was prepared by C. B. Holder of this Laboratory.[5] This labeled material was diluted with Matheson pure grade *n*-heptane.[6]

Methyl-labeled Toluene.—The C^{14} assay procedure was calibrated with Tracerlab methyl-labeled toluene (lot 16-4-1).

Catalyst.—The catalyst[7] was 14.4% Cr_2O_3, 1.08% K_2O and 0.64% Ce_2O_3 by weight on γ-Al_2O_3. It had a specific surface area of 60 m.^{2}/g.

Apparatus.—The *n*-heptane-1-C^{14} charge was displaced from a buret by slowly raising the level of a mercury column at the bottom of the buret. The charge went directly to an 18–8 stainless steel preheater tube packed with stainless-steel wool. It then passed over the catalyst in an 18–8 stainless steel reactor tube which contained an internal concentric thermocouple well. The products were condensed, first by a water-cooled condenser and then by a Dry Ice–isopropyl alcohol cooled knockback condenser.

Reaction Conditions.—Two runs were made at atmospheric pressure and 490°, but with different charge rates. The first run was made over 56.8 g. of catalyst. The catalyst was first reduced with H_2 at 490°. Then a total of 138 g. of *n*-heptane-1-C^{14} was charged at 23 ml./hr. with reactor temperature held between 486 and 495°. Distillation of the 118.6 g. of liquid product in a concentric-tube column recovered 37.4 g. of toluene. These same conditions had been shown with ordinary *n*-heptane to yield a liquid product, for which mass spectrometric analysis on the unseparated product indicated a toluene content of 56 mole per cent. The second run was made over 54.8 g. of catalyst held between 487 and 494°. A total of 22.0 g. of *n*-heptane-1-C^{14} was charged at 9.5 ml./hr.; 16.6 g. of liquid product was recovered and 8.1 g. of toluene distilled from it. Under these same conditions, a run with ordinary *n*-heptane gave a liquid product which contained 74 mole per cent. toluene.

Radioactive Assay of Liquids and Solids.—Samples were burned in a Pregl-type combustion train, and the resulting CO_2 was collected in a liquid nitrogen-cooled trap, distilled once from Dry Ice–isopropyl alcohol temperature in order to remove water, and transferred by vacuum distillation to an ionization chamber.[8] The pressure in the chamber was raised to atmospheric by the addition of ordinary CO_2, and the C^{14} activity determined by measuring the rate of charge accumulation by means of a vibrating-reed electrometer.

Radioactive Assay of the Toluene Methyl Group.[9]—A 3-ml. portion of toluene was refluxed with a solution of 15 g. of $KMnO_4$, 80 ml. of water and 3 drops of 10% NaOH solution with vigorous stirring for 6 to 8 hours. The mixture was cooled, and 14 g. of anhydrous Na_2SO_3 was added. The mixture was reheated to reflux temperature, and 6 *N* H_2SO_4 was added until a clear solution was obtained. The hot solution was poured into a beaker, allowed to cool to room temperature, and then chilled to 0°. The resulting crystals were filtered out on a fritted-glass filter and then were air-dried. A small portion was recrystallized from water to serve as benzoic acid for C^{14} assay. The remaining crystals were taken up in 30 ml. of 1 *N* NaOH. This solution was warmed, and to it was added 5.1 g. of $AgNO_3$ dissolved in 20 ml. of hot water. The resulting precipitate was dried at 100°, then added, together with 50 ml. of CCl_4, to a three-necked flask. This mixture was stirred vigorously and brought to reflux temperature. Then 60 ml. of 0.5 *N* Br_2 in CCl_4 was added dropwise while N_2 gas was swept over the refluxing mixture. The CCl_4 and Br_2 were condensed out of the gas stream by a water-cooled condenser followed by a Dry Ice–isopropyl alcohol cooled trap. The CO_2 in the gas stream was collected in a liquid nitrogen-cooled trap and assayed for C^{14} activity in the same way as the CO_2 from combustion.

Results

The C^{14} activity per unit weight of carbon relative to an arbitrary value of 100 for the toluene in each run is shown in Table I. Two independent assay series were run on each product and the uncertainties shown with the experimental values are simply the standard deviation calculated from the two values. In one case, one assay was lost so no deviation is shown.

The percentage of the C^{14} in the product toluene which was present in the methyl group is shown in Table II as calculated from the results of Table I. Two methods of calculation were used. In one it was assumed that, in the Tracerlab product, C^{14} was located only in the methyl position so that the ratio of the CO_2 specific radioactivity from the methyl group to the specific radioactivity of the toluene as a whole was the ratio one would get by this assay procedure for 100% methyl-labeled

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[2] R. C. Pitkethly and H. Steiner, *Trans. Faraday Soc.*, **35**, 979, 1006 (1939).

[3] E. F. G. Herington and E. K. Rideal, *Proc. Roy. Soc.* (*London*) **184A**, 434, 447 (1945).

[4] R. W. Wheatcroft, Dissertation, Univ. of California, August 1, 1949.

[5] *n*-Hexylmagnesium bromide was carbonated with labeled CO_2. The resulting acid was reduced directly with $LiAlH_4$ to the alcohol. The tosyl ester of the alcohol was reduced with $LiAlH_4$ to give *n*-heptane-1-C^{14}. A small amount of inactive toluene formed was removed by silica gel adsorption. It is believed that this toluene was the result of the reduction of the *p*-toluenesulfonic acid part of the ester or unesterified *p*-toluenesulfonyl chloride present as impurity in the ester.

[6] Mass spectrometric analysis showed only *n*-heptane present.

[7] The catalyst was prepared by Leon W. Cook of this laboratory.

[8] The chambers and the measuring method are described in J. J. Mitchell, *J. Chem. Phys.*, **21**, 1153 (1953).

[9] This method was adapted from that of R. W. Wheatcroft (see ref. 4).

TABLE I

RELATIVE[a] SPECIFIC RADIOACTIVITY

Material	Tracerlab toluene-C^{14}-7	Low conversion aromatization	High conversion aromatization	Average
Starting *n*-heptane-C^{14}-1	....	101.3 ± 1.2	96.8 ± 1.8	99.0 ± 2.8
Benzoic acid	93.8 ± 1.9	94.4	98.5 ± 1.5	95.6 ± 1.5
Methyl CO_2	634 ± 22	174 ± 2	181 ± 0	....

[a] These values are 100 times the ratio of the specific activity of the product in question to the specific activity of the toluene in the same run. These were, in units of millivolts per chart division per millimole of carbon (see ref. 8), 2950 for Tracerlab toluene, 780 for low conversion toluene and 800 for high conversion toluene. The Tracerlab toluene, as used, contained about 0.2 millicurie of C^{14} per mole of toluene.

TABLE II

PERCENTAGE LABEL IN METHYL GROUP

Basis of calculation	Methyl label, %		
	Tracerlab toluene-C^{14}-7	Low conversion toluene	High conversion toluene
Tracerlab product	100	27.4 ± 1.0	28.6 ± 1.0
Relative spec. act. for methyl CO_2	90.6 ± 3.1	24.8 ± 0.3	25.9 ± 0

toluene. This same ratio for the aromatization toluene divided by that for the Tracerlab toluene then gives, when multiplied by 100, the percentage of methyl label in the aromatization toluene.

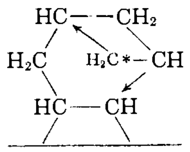
The other method is based on the fact that toluene has 7 carbon atoms so that, if all the radioactivity in the toluene were located in the methyl group, the activity per unit weight of carbon in the methyl group would be 7 times as great as that of the toluene as a whole. This is straightforward and would be the preferable method if one could be sure that no isotope discrimination occurred in the assay procedure. Table I shows that the catalytic dehydrocyclization showed no isotope discrimination within experimental error. On the other hand, the oxidation of toluene to benzoic acid caused an apparent 4% decrease in specific activity. If one assumes that the Tracerlab toluene is 100% methyl labeled, then the assay[10] of the methyl carbon involves an over-all 10% isotope discrimination.

If one averages all four results in the two dehydrocyclization runs, one obtains 26.7 ± 1.7% methyl label. While this procedure ignores the difference between the two methods of calculation, it makes clear the fact that the percentage of methyl label was the same within a 10% error for the low and high conversion and was not the 50% predicted by the three mechanisms described earlier.

Discussion

Wheatcroft[4] did a similar experiment with 1-heptene-1-C^{14} in which he increased contact time with the catalyst, thereby obtaining increasing percentages of toluene in the product. With a product containing 35 mole per cent. toluene, he found 17% methyl label in the toluene; with 60 mole per cent. toluene, he found 26% methyl label; and, with 74 mole per cent., he found 33% methyl label. He argued that these values lay on a straight line which predicted 50% label for a product consisting of 100% toluene. His reaction mechanism postulated that, when double bond migration had reached an equilibrium state, one would find 50% methyl-labeled toluene, so he felt he had demonstrated the validity of his mechanism. However, it is apparent that what he showed was that, with a contact time long enough to give 60 mole per cent. toluene in the product, double-bond migration had brought the 1-heptene-1-C^{14} to the same state as dehydrogenated *n*-heptane-1-C^{14}.

There are at least two reasonable mechanisms which can be postulated which lead to conversion of *n*-heptane-1-C^{14} to 25% methyl-labeled toluene. One of these is based on Herington and Rideal's[3] explanation of the product distribution from the dehydrocyclization of *n*-octane. They postulate the formation of a transannular bridge which breaks when the adsorbed saturated cyclic intermediate desorbs and dehydrogenates simultaneously. In analogy, if 1-heptene is the species which chemisorbs in the production of toluene, one can argue that a transannular bridge forms to give either



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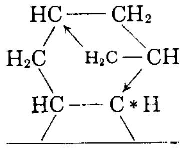
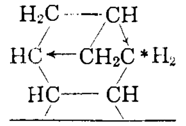


depending on whether 1-heptene-1-C^{14} or 1-heptene-7-C^{14} was adsorbed. The arrows show the bonds formed when the rings close, and the asterisks show the location of the C^{14} in the labeled molecules. If one argues that the breaking of any of the four bonds in the four-membered ring is equally probable in the dehydrogenation step, he finds that the postulation of equal quantities of these two chemisorbed species leads to 25% methyl-labeled toluene. It should be noted that one should also find in the product 50% *ortho*-labeled and 25% *para*-labeled toluene.

The same distribution arises from 2-heptene, if one assumes that the transannular bridge always closes to a carbon not attached to the catalyst, since the intermediates will then be either



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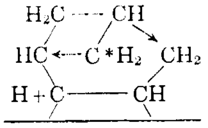

Experimentation with Courtauld models indicates that this bridge is quite feasible as indeed one would expect from the existence of terpenes. However, there is another possible mechanism, similar to that postulated by Pines and Myerholtz,[11] which also predicts a 25% yield of methyl-

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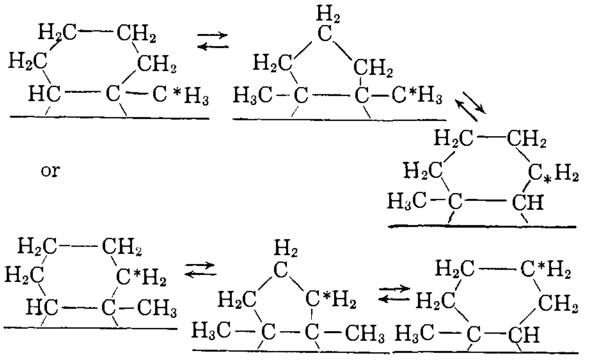
[10] The best yield of benzoic acid from toluene was 57 mole per cent. The yield of the decarboxylation step on the basis of trials with C.P. benzoic acid was 72 mole per cent. The average over-all mole per cent. yield of CO_2 on the basis of starting toluene in seven radioactivity assay runs was 28.7 ± 9.5. The other assays involved the complete combustion of the sample and so did not give the possibility of isotope discrimination.

[11] H. Pines and R. W. Myerholtz, Jr., THIS JOURNAL, **77**, 5392 (1955).

labeled toluene. They used the mechanism to explain the shift in label in methyl-C^{14}-cyclohexane over activated aluminum bromide at low temperature. To extend their mechanism to the dehydrocyclization conditions one assumes that rapid ring contraction and expansion occurs at 490° and that only the adsorbed methylcyclohexene species can desorb and dehydrogenate to toluene. Thus, for 2-heptene, one can write



depending on whether 2-heptene-C^{14}-1 or 2-heptene-C^{14}-7 is adsorbed. The assumption of the equal concentration and equal desorption probability of these four varieties of methyl cyclohexene leads to a prediction of 25% methyl-labeled toluene, 25% *o*-labelled, 25% *m*-labeled and 25% *p*-labeled.

One could argue that the 1-heptene is converted to toluene by simple ring closure but at a slower rate so as to contribute enough methyl-labeled toluene to raise the 25% to about 30%.

On the other hand, one could equally well reverse the role of the two olefins by arguing that adsorbed methylcyclohexene underwent a ring expansion to adsorbed cycloheptene. Then 1-heptene would yield equal proportions of methyl-, *o*-, *m*- and *p*-labeled toluene, and 2-heptene might be expected to give equal proportions of methyl-*o*-labeled toluene.

These speculations remain just that unless one can distinguish which mechanism is operating. It is interesting to note that schemes[12,13] now exist for assay of the radioactivity of the ring carbons in toluene. An assay of the C^{14} content of the *m*-position by one of these methods would allow one to distinguish between the transannular bridge and ring expansion and contraction mechanisms because the first predicts no *m*-labeled toluene and the second 25% *m*-labeled toluene.

Acknowledgment.—The author wishes to thank Dr. R. P. Eischens for suggesting this problem and Messrs. A. K. Blom and E. G. Northrop for their aid with the experimental work.

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[13] J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, THIS JOURNAL, **78**, 601 (1956).

BEACON, N. Y.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Bis-(β-diketones). II. The Synthesis and Spectra of Compounds of the Type [(RCO)R'COCH]$_2$CHR''[1,2]

BY DEAN F. MARTIN, MAURICE SHAMMA AND W. CONARD FERNELIUS

RECEIVED JUNE 6, 1958

A number of new bis-(β-diketones) of the type [(RCO)(R'CO)CH]$_2$CHR'' have been prepared: R = R' = CH_3, R'' = $(CH_2)_5CH_3$, 2-ClC_6H_4, 2-$CH_3OC_6H_4$, 4-$CH_3OC_6H_4$, 4-$(CH_3)_2NC_6H_4$, 3,4-$CH_2O_2C_6H_3$, 2-C_5H_4N, 3-C_5H_4N, 4-C_5H_4N-; R = CH_3, R' = CH_3OCH_2, R'' = C_6H_5, 4-$CH_3OC_6H_4$, 4-HOC_6H_4, 3,4-$CH_2O_2C_6H_3$, 4-$(CH_3)_2NC_6H_4$, 2-C_5H_4N, 4-C_5H_4N. These bis-(β-diketones) were prepared by the condensation of a β-diketone, $RCOCH_2COR'$, with an appropriate aldehyde in a 2:1 molar ratio. The condensation was not successful for β-diketones containing a trifluoroacetyl group. The infrared and ultraviolet absorption spectra of the bis-(β-diketones) are recorded.

Introduction

In continuation of an investigation into the chelation behavior of bis-(β-diketones),[3,4] several new compounds of the type [(RCO)(R'CO)CH]$_2$CHR'' have been prepared by the interaction of a β-diketone of the type $RCOCH_2COR'$, and an aldehyde, R''CHO, in the presence of a suitable catalyst. Previous investigators have reported the synthesis of the compounds where R = R' = CH_3, R'' = H,[5] R'' = CH_3,[5] R'' = 3-CH_3O–4-OH–C_6H_3,[6] and R'' = C_6H_5[7,8]; R = CH_3, R' = C_6H_5, R'' = H,[9] R'' = CH_3,[10] R'' = C_6H_5,[11] and R'' = 3-$O_2NC_6H_3$[12]; R = R' = C_6H_5, R'' = H,[13,14] and R'' = C_6H_5.[15]

There are reported here the syntheses and proper-

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[1] This research was supported in whole by the United States Air Force under Contact AF 33(616)-2742, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] Based upon a portion of the doctoral dissertation of Dean F. Martin, The Pennsylvania State University, 1958.

[3] E. H. Holst, Doctoral Dissertation, The Pennsylvania State University, August, 1955.

[4] D. F. Martin, M. Shamma and W. C. Fernelius, THIS JOURNAL, **80**, 4891 (1958).

[5] E. Knoevenagel, *et al.*, *Ber.*, **36**, 2136 (1903).

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